

Preliminary measurements of summer nitric acid and ammonia concentrations in the Lake Tahoe Basin air-shed: implications for dry deposition of atmospheric nitrogen

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“Capsule”: Dry deposition of nitric acid is the major input of nitrogen in the Lake Tahoe Basin.

Abstract

Over the past 50 years, Lake Tahoe, an alpine lake located in the Sierra Nevada mountains on the border between California and Nevada, has seen a decline in water clarity. With significant urbanization within its borders and major urban areas 130 km upwind of the prevailing synoptic airflow, it is believed the Lake Tahoe Basin is receiving substantial nitrogen (N) input via atmospheric deposition during summer and fall. We present preliminary inferential flux estimates to both lake surface and forest canopy based on empirical measurements of ambient nitric acid (HNO₃), ammonia (NH₃), and ammonium nitrate (NH₄NO₃) concentrations, in an effort to identify the major contributors to and ranges of atmospheric dry N deposition to the Lake Tahoe Basin. Total flux from dry deposition ranges from 1.2 to 8.6 kg N ha⁻¹ for the summer and fall dry season and is significantly higher than wet deposition, which ranges from 1.7 to 2.9 kg N ha⁻¹ year⁻¹. These preliminary results suggest that dry deposition of HNO₃ is the major source of atmospheric N deposition for the Lake Tahoe Basin, and that overall N deposition is similar in magnitude to deposition reported for sites exposed to moderate N pollution in the southern California mountains. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Background

The Lake Tahoe Basin is a high elevation (1898 m), bowl-shaped watershed (1343 km²) dominated by Lake Tahoe (512 km²). Lake Tahoe is known for its exceptional clarity, which is maintained by virtue of a low watershed to lake surface area ratio. The surrounding nitrogen (N)-limited forest ecosystem takes up most nutrients [e.g. N and phosphorus (P)] in runoff before they reach the lake (Goldman, 1988; Aber et al., 1989; Fenn et al., 1998). This low flux of nutrients to the lake leads to low primary productivity (i.e. algal and phytoplankton growth) and exceptionally clear water (Goldman, 1988), which make Lake Tahoe one of the most scenic lakes in the world.

Lake Tahoe lies only 230 km east (downwind of prevailing westerlies) of the San Francisco metropolitan area and 130 km east of the Sacramento metropolitan area. Both areas are significant sources of pollutant emissions (McColl and Bush, 1978; McColl, 1982). The clarity of Lake Tahoe has declined by 30% over the past 50 years, which Goldman (1988) attributes to N and P inputs. Jassby et al. (1994) attribute the bulk of N inputs to atmospheric deposition; however the specific types of deposition (dry vs. wet), their sources (in-basin vs. out-of-basin), and the magnitude of their influence on aquatic and terrestrial portions of the ecosystem have not been investigated.

Studies in the southern Sierra Nevada Mountains, the eastern United States, and Europe provide insight into modes and magnitudes of atmospheric N deposition most likely to be found in the Lake Tahoe Basin. Sites in The Netherlands receive up to 100 kg N ha⁻¹ year⁻¹, with 40–60% as dry deposition, and significant

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proportions of that from ammonium nitrate aerosol (NH_4NO_3), ammonia gas (NH_3), and nitric acid gas (HNO_3 ; Lindberg et al., 1990; Pearson and Stewart, 1993). The eastern United States has lower total N deposition (upper limits of $30 \text{ kg N ha}^{-1} \text{ year}^{-1}$) but similar proportions of wet to dry deposition (Lindberg et al., 1986). Regions in the more arid western USA experience less N deposition, with the exception of areas within downwind plumes of urban and agricultural areas. Climate in the Sierra Nevada Mountains, on the other hand, is characterized by warm, dry summers and wet, cool winters, which gives rise to different deposition regimes than those in the east. Studies in the arid San Bernardino Mountains downwind of Los Angeles show that dry N deposition dominates atmospheric inputs, with HNO_3 , NH_3 , and NH_4NO_3 contributing the bulk of total atmospheric N ($9.0\text{--}30 \text{ kg N ha}^{-1} \text{ year}^{-1}$; Taylor et al., 1997; Bytnerowicz et al., 1996; Fenn et al., 1998).

HNO_3 and NH_4NO_3 are secondary pollutants, so the urban areas responsible for elevated N deposition in arid mountain environments like the San Bernardino Mountains and the Lake Tahoe Basin do not directly emit HNO_3 or NH_4NO_3 . Instead N as NO_x is emitted to the atmosphere and undergoes photochemical transformation to HNO_3 during transport. HNO_3 and NH_3 (a primary pollutant) can in turn react to form an equilibrium with NH_4NO_3 . Emission of NO_x and deposition of the resultant secondary pollutants (i.e. HNO_3 and NH_4NO_3) are thus separated in time and space. This means that pollutants may deposit hundreds of miles from their emission point, on the order of hours to days after their emission (Singh, 1987). During the summer and fall, N as NO_x and NH_4NO_3 may be transported by prevailing westerly and southwesterly winds and deposited within the Lake Tahoe Basin (Cahill et al., 1996). In addition, local development and traffic emissions (i.e. NO_x) may contribute to the formation of local N pollutants, especially during inversion events which provide enough time for the photochemical production of HNO_3 (Cahill et al., 1978; Singh, 1987).

Winter N deposition in the Lake Tahoe Basin is dominated by wet deposition. Prevailing westerlies bring pristine Pacific air masses into the Lake Tahoe Basin, while pollutants in the upwind California central valley are retained under strong inversions that characterize central valley climate in the winter (Cahill et al., 1978). Wet deposition in and around the Lake Tahoe Basin has been characterized, amounting to $1.7\text{--}2.9 \text{ kg N ha}^{-1} \text{ year}^{-1}$ (Jassby et al., 1994; NADP, 1996), which is low compared to more polluted US and European sites.

2. Objective

In this preliminary study, we hypothesized that HNO_3 , NH_3 , and NH_4NO_3 are sources of atmospheric

N deposition in the Lake Tahoe Basin during the summer and fall dry season. To determine their relative importance, we measured HNO_3 and NH_3 concentrations, and obtained data for NH_4NO_3 from the Inter-agency Monitoring of Protected Visual Environments (IMPROVE) network data (Cahill, 1999) over the 3-month summer and fall dry seasons in 1997 and 1998. We then coupled the concentration data with inferential methods to estimate dry HNO_3 , NH_3 , and NH_4NO_3 fluxes (as N) to both water surfaces and forest canopies. The study's overall objective was to quantify upper and lower limits for dry N flux to lake surface water and forest canopies in the Lake Tahoe Basin. From these preliminary investigations, we evaluated relative contribution of each species, so that the most important N species with respect to N flux could be targeted for more intensive research.

3. Experimental methods

3.1. Field measurements

We conducted each dry season's sampling campaign at two sites in the Lake Tahoe Basin, during dry periods characteristic of Lake Tahoe Basin summer and fall ($n=30$, July through September 1997 and 1998). We focused this campaign on deposition to forest canopies, selecting two sites on opposite sides of the lake and at significant elevation above the lake. The western site was at Bliss State Park (Fig. 1), adjacent to Desolation

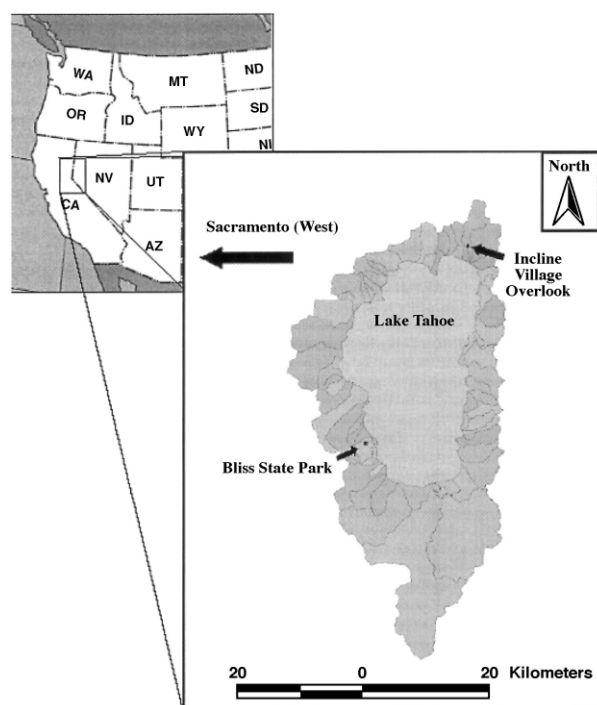


Fig. 1. Location of sampling sites in the Lake Tahoe Basin.

Wilderness at an elevation of 2135 m (237 m above lake level). The eastern site was at Incline overlook, located on the southwest exposure of Mt. Rose, at a 2440 m elevation (542 m above lake level). Both sites were chosen in open terrain to represent ambient concentrations above forest canopies and to minimize boundary layer turbulence. At both sites, trees were less than 10 m tall, spaced at least 5 m from the site.

A large part of the uncertainty in deposition estimates stems from uncertainties in leaf area index (LAI). No formal estimates for LAI values exist for the Lake Tahoe Basin, so LAI was estimated by measuring diameter at breast height for several representative plots in the Lake Tahoe Basin and relating that data by species-specific regression equations to leaf biomass (Kercher and Axelrod, 1984). Leaf biomass was then related to leaf surface area (all sided), with species-specific allometric relationships derived from locally grown seedlings.

Air was sampled over 8–12-h periods at a height of 2 m and a flow rate of 10 l min⁻¹. Each day sample was immediately followed or preceded by a night sample. Particulate matter was removed, but not collected, by 2.5 µm cutpoint cyclones while annular denuders (University Research Glassware, Research Triangle Park, NC, USA) simultaneously collected gaseous NH₃ and HNO₃. When coated with citric acid and sodium carbonate, these denuders collect NH₃ and HNO₃, respectively, with high efficiency (Allegrini et al., 1987; USEPA, 1989). Duplicate samples ($n=4$) had standard errors of 0.76 nmol N m⁻³ (HNO₃) and 1.2 nmol N m⁻³ (NH₃, Table 1). The standard errors for duplicate samples were used as a measure of the experimental precision, whereas standard errors for repeated measurements from summer and fall 1997–1998 represent the method's accuracy in estimating mean dry season concentrations.

3.2. Laboratory analysis

Following collection, samples were refrigerated at 5°C. To extract the HNO₃ denuders, 10 ml of double deionized water were added, denuders rotated and

inverted to ensure mixing, and the solution decanted into a clean 40-ml Nalgene polyethylene vial. Sample analysis was performed with a Dionex Ion Chromatograph using spectrophotometric detection at 210 nm (USEPA, 1989). Samples were injected directly from the storage vial into the sample loop and run through an AS4A column with a sodium bicarbonate/carbonate eluent. Blank absorbance was subtracted from sample absorbance, and HNO₃ concentration determined by regression using NaNO₃ as a standard. All samples were analyzed within 30 days, and were checked against National Institute of Standards and Technology (NIST) certified standards (Environmental Resource Associates, Arvada, CO, USA). The mean air concentration (nmol N as HNO₃ m⁻³) for each sampling period was calculated by dividing the total moles of N in each denuder by the volume of air sampled.

Ammonia denuders were transported, refrigerated, and extracted in the same manner. Indophenol blue colorimetric methods were used to determine sample air concentrations (Lind, 1985). Each sample was rinsed from storage bottles into borosilicate glass graduated cylinders and diluted to 25 ml (the volume necessary for calorimetry). After reagents were added, color was allowed to develop for 1 h, but no more than 12 h, after which aliquots of well-mixed solution were transferred to 1-cm path-length cuvettes and analyzed in a Shimadzu UV-1201 Spectrophotometer. Using NIST-based regression against NH₄SO₄ standards, concentrations of NH₄⁺ in solution were estimated and then total NH₃ (in air) was calculated. The total amount in the sample denuder (nmol N as NH₃) was divided by total volume of air sampled (m³) to estimate the mean air concentration for the period sampled (nmol N m⁻³). Limits of detection for both NH₃ and HNO₃ were defined as twice the value of the highest blank for each individual analysis and species (Table 1).

3.3. Data analysis

3.3.1. Estimates of flux to forest canopies

Forest canopy structure and physiology play key roles in determining pollutant flux to forested watersheds (Taylor et al., 1994). Dry N deposition to forest canopies can be inferred according to Eq. (1) (Hanson and Lindberg, 1991; Hanson et al., 1992):

$$F_c = V_d(C_z - C_0), \quad (1)$$

where F_c , flux to canopy (nmol N m⁻² s⁻¹); C_z , concentration at the height of measurement (nmol N m⁻³); C_0 , concentration at the site of assimilation (nmol N m⁻³); V_d , the canopy-scale deposition velocity (m s⁻¹).

For HNO₃ and NH₄NO₃, canopy-scale deposition velocities (V_d) values vary by factors of 10, depending on environmental conditions, boundary layer thickness,

Table 1
Concentrations of N-containing gases in the Lake Tahoe Basin (± 1 S.E.)^a

| Ni species | Mean daytime concentration (nmol- N m ⁻³ , ±1 S.E.) | Mean night-time concentration (nmol- N m ⁻³ , ±1 S.E.) | Detection limits (nmol N m ⁻³) |
|---------------------------------|--|---|--|
| HNO ₃ | 26 (±2.9) | 11 (±1.5) | 4.9 |
| NH ₃ | 20 (±3.8) | 49 (±12) | 17 |
| NH ₄ NO ₃ | 7.2 (±0.50) | 7.2 (±0.50) | 0.49 |

^a NH₃ and HNO₃ were measured during the summer and fall of 1997–1998, whereas NH₄NO₃ was compiled from IMPROVE network data from the summer and fall of 1990–1996 (Cahill, 1999).

and species/canopy type (Slinn, 1982; Lindberg et al., 1986, 1990; Baldocchi, 1991). LAI, a measure of the canopy leaf surface area relative to the ground surface area ($\text{m}^2 \text{m}^{-2}$), is also one of the most significant sources of this variation. An average LAI of 6 was used for all calculations. This value represents all-sided leaf surface area in the forest canopy, calculated by multiplying projected (one-sided leaf area) by 2.6 (Körner, 1995). One way of normalizing for variation due to LAI is to multiply leaf-level deposition velocities (V_g ; Eq. (3)) by LAI (Eq. (2)), yielding a whole canopy V_d (Hanson et al., 1989; Hanson and Lindberg, 1991):

$$V_d = V_g \times \text{LAI}; \quad (2)$$

$$V_g = \frac{J_{\text{leaf}}}{(C_a - C_i)}, \quad (3)$$

where J_{leaf} , flux to leaf ($\text{nmol m}^{-2} \text{s}^{-1}$); V_g , leaf-level deposition velocity (m s^{-1}); V_d , canopy-level deposition velocity (m s^{-1}); C_a , ambient concentration of the pollutant (nmol m^{-3}); C_i , surface concentrations of the pollutant at the site of assimilation/reaction (nmol m^{-3}); LAI, all-sided leaf surface area ($\text{m}^2 \text{canopy m}^{-2}$ -ground). Leaf-level deposition velocities (V_g) used to calculate canopy-level deposition velocities (V_d) are reported in Table 2.

Leaf-level values for NH_3 deposition velocities (V_g) also vary widely in the literature, largely because of different theories about the sites and mechanisms for NH_3 deposition and emission. Sutton et al. (1998) proposed that NH_3 deposits to the thin water films on the leaf cuticle, which acts as a capacitor, storing the NH_3 that can either be taken up by the plant or revolatilized. In such a case relative humidity would play an important role in determining V_g . Schjørring et al. (1998) proposed that deposition occurs on the surface of leaf mesophyll cells, within the substomatal cavities. In the Lake Tahoe Basin, temperatures typically reached 15°C

during the day, while relative humidities generally stayed below 30%, so any thin water films formed would evaporate the next day, revolatilizing any NH_3 deposited therein. We assume that on a monthly time scale deposition to cuticular water films is a temporary phenomenon, that any NH_3 stored in such water films were revolatilized when they evaporated, and that this revolatilized NH_3 ultimately deposited to mesophyll in the leaf interior.

3.3.2. Calculating canopy-level NH_3 compensation points (C_0)

Leaf mesophyll cells contain aqueous NH_4^+ , a biochemically important compound present in the apoplasm of leaf mesophyll cells. This aqueous NH_4^+ exists in equilibrium with gaseous NH_3 in the surrounding substomatal cavities, an equilibrium governed by Henry's Law. The following equation predicts the gas-to-liquid phase distribution of NH_3 :

$$P_{\text{NH}_3} = RT(10^{1.60352-4207.62/T}) \left(\frac{[\text{NH}_4^+]_{\text{solution}}}{[\text{H}^+]} \right), \quad (4)$$

where $[\text{NH}_4^+]$, apoplastic NH_4^+ concentration ($46 \mu\text{mol l}^{-1}$); $[\text{H}^+]$, $10^{-6.8} \text{H}^+$ concentration ($-\text{Log pH}$) (mol l^{-1}); R , $0.0831 \text{ L atm mol}^{-1} \text{ }^\circ\text{K}^{-1}$; T , ambient temperature ($^\circ\text{K}$); P_{NH_3} , partial pressure (ppbv) of ammonia in the substomatal cavity. This equation describes an NH_3 compensation point, above which deposition occurs, and below which emission occurs (Farquhar et al., 1980).

Langford and Fehsenfeld (1992) applied this equation to trees at the canopy scale, finding that this equilibrium equation accurately predicted NH_3 concentrations over forested terrain under pristine conditions. This suggests that Henry's Law (Eq. (4)) predicts not only substomatal NH_3 partial pressures, but compensation points (C_0) at the canopy level as well, and that such compensation points are temperature dependent. Extrapolating from vegetation compensation points measured at one temperature, Husted and Schjørring (1996) calculated compensation points at other temperatures using the following modified Claysius–Clayron equation (Atkins, 1990):

$$p = p^* e^{-C} \\ C = \left[\frac{\Delta H_{\text{dis}}^\circ + \Delta H_{\text{vap}}^\circ}{R} \times \left(\frac{1}{T} - \frac{1}{T^*} \right) \right], \quad (5)$$

where $\Delta H_{\text{dis}}^\circ$, $52.21 \text{ kJ mol}^{-1}$; $\Delta H_{\text{vap}}^\circ$, $34.18 \text{ kJ mol}^{-1}$; T^* , the known temperature (293°K — Langford and Fehsenfeld, 1992); T , the unknown temperature ($^\circ\text{K}$); p^* , known partial pressure of the gas (ppbv); p , new partial pressure at the new temperature (ppbv). R , 8.314

Table 2

Leaf-level deposition velocity (V_g) values used in calculating dry N deposition to forest canopies in the Lake Tahoe Basin

| N species | Minimum leaf conductance (V_g , mm s^{-1}) | Maximum leaf conductance (V_g , mm s^{-1}) | References |
|--------------------------|---|---|--|
| HNO_3 | 2.0 | 12 | Dasch, 1987, 1989; Cadle et al., 1991 |
| NH_3 | 4.0 | 8.0 | Langford and Fehsenfeld, 1992; Sorteburg and Øystein, 1996 |
| NH_4NO_3 | 0.1 | 1.0 | Lin et al., 1993; Nicholson, 1988; Slinn, 1982 |

(J mol⁻¹ K⁻¹). Langford and Fehsenfeld observed a forest compensation point of 0.8 ppbv at 20°C (p^* , Eq. (5)), a reasonable value for non-crop species (Schjørring et al., 1998). Assuming that this compensation point applied to the forested terrain of the Lake Tahoe Basin, we used temperature data measured simultaneously with our NH₃ data to calculate NH₃ compensation points. This compensation point (ppbv) was converted to nmol m⁻³ and used as surface concentration (C_0). Subtracting this surface concentration from ambient concentrations yielded an estimate of the concentration gradient that drives NH₃ deposition to the forest canopy (Fig. 2).

3.4. Estimates of flux to the surface of Lake Tahoe

Deposition to water surfaces is less complex than that of forest canopies, since the surface is homogeneous and since C_0 for any of these N species is negligible, especially in ultra-oligotrophic Lake Tahoe (Goldman, 1988). However, studies detailing deposition velocities (V_d) to water are few. Hertel et al. (1995) and Lee et al. (1998) both arrived at an HNO₃ deposition velocity of 6.4 mm s⁻¹ to water. A comparable range of 1.5–7.6 mm s⁻¹ was found for NH₃ by Sorteburg and Øystein (1996). Another study by Slinn (1982) reported much lower NH₄NO₃ V_d values, from 0.05 to 2.0 mm s⁻¹. These deposition velocities (Table 3) were used to calculate flux to Lake Tahoe surface water as follows:

$$F_w = V_d \times C_a, \quad (6)$$

where F_w , flux to lake surface in nmol N m⁻² s⁻¹; C_a , concentration measured at either Bliss or Incline site (nmol N m⁻³); V_d , the deposition velocity in units of m s⁻¹.

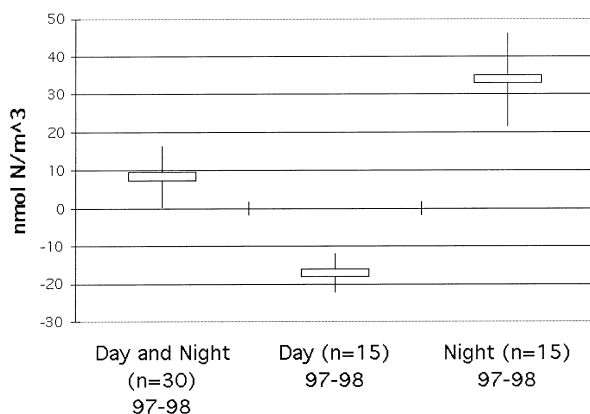


Fig. 2. Calculated NH₃ concentration gradients. Temperature-dependent compensation points were subtracted from measured NH₃ concentrations (Table 1) to represent the NH₃ concentration gradient between the forest canopy and the boundary layer above Eq. (1). Bars represent ± 1 S.E. of mean concentration; boxes represent ± 1 S.E. of duplicate samples.

Table 3

Deposition velocity (V_d) values used in calculating direct dry N deposition to Lake Tahoe

| N species | Minimum deposition velocity (V_d , mm s ⁻¹) | Maximum deposition velocity (V_d , mm s ⁻¹) | References |
|---------------------------------|--|--|--|
| HNO ₃ | 6.4 | 6.4 | Hertel et al., 1995; Lee et al., 1998 |
| NH ₃ | 1.5 | 7.6 | Hertel et al., 1995; Sorteburg and Øystein, 1996; Lee et al., 1998 |
| NH ₄ NO ₃ | 0.05 | 2.0 | Slinn, 1982; Hertel et al., 1995; Lee et al., 1998 |

4. Results and discussion

4.1. Ranges and diurnal variation in HNO₃ and NH₃ concentrations

Gas phase HNO₃ concentrations ranged (± 1 S.E.) from 24 to 29 nmol N m⁻³ during the daytime ($n=15$), and from 9.7 to 13 nmol N m⁻³ during the night ($n=15$) from July through September of 1997 and 1998 (Table 1). Mean night-time HNO₃ concentrations were twice continental background, and mean daytime HNO₃ concentrations were four times continental background (Singh, 1987; Atlas et al., 1992; Bytnerowicz and Fenn, 1996). Standard errors for HNO₃ measurements during the day were 2.9 and 1.5 nmol m⁻³ at night.

Ammonia exhibited the opposite diurnal pattern, with daytime ranges from 16.5 to 24.0 nmol N m⁻³ that were close to continental background, and night-time ranges from 36.4 to 60.6 nmol N m⁻³ that were three times continental background (Langford and Fehsenfeld, 1992). Daytime compensation points calculated for forest canopies exceeded actual NH₃ concentrations, suggesting that NH₃ emission occurred (Fig. 2) and that the forest canopies were the NH₃ source. Conversely, the high night-time variability observed suggests a night-time source for NH₃. Although NH₄NO₃ concentrations were low, particle-to-gas conversion or influences from nearby urban areas may be responsible for these higher, more variable values (Huebert et al., 1988). Particle-to-gas conversion could not be confirmed by NH₄NO₃ measurements since IMPROVE samplers run on a 24 h schedule and are not suitable for day/night comparisons. Additionally, most of the elevated NH₃ concentrations contributing to this high variability occurred during the 1997 measurements, when only six out of 24 measurements were taken, which suggests that an isolated event could also have biased our data (Fig. 3).

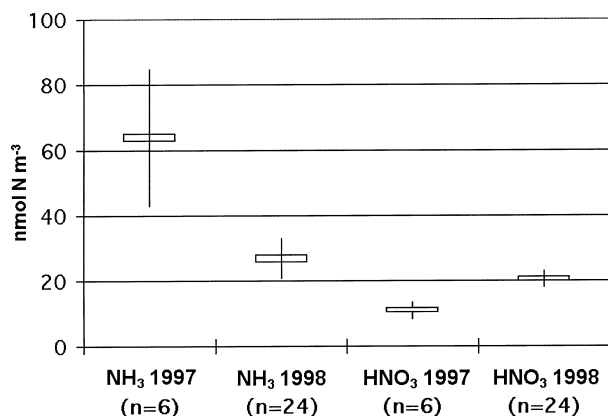


Fig. 3. Concentrations of HNO_3 and NH_3 during dry season of 1997 compared to those in 1998. Bars represent ± 1 S.E. of mean concentration; boxes represent ± 1 S.E. of duplicate samples.

4.2. N fluxes to forest canopies

Compared to the range of annual wet N deposition ($1.7\text{--}2.9 \text{ kg N ha}^{-1} \text{ year}^{-1}$), the range of dry N deposition to forest canopies during the summer and fall dry season ($1.2\text{--}8.6 \text{ kg N ha}^{-1}$) was substantial (Table 4). Ammonia contributed minimal amounts of N, largely because compensation point often exceeded concentration (Fig. 2). Net NH_3 deposition was close to zero ($0.2\text{--}0.9 \text{ kg N ha}^{-1}$) as a result. Fluxes from NH_4NO_3 were also minimal and varied from 0.03 to 0.2 kg N ha^{-1} . Nitric acid was the largest contributor, depositing $1.0\text{--}7.6 \text{ kg N ha}^{-1}$ over the 3-month period. We conclude from this that NH_4NO_3 and NH_3 deposition to forest canopies during the summer and fall were likely negligible, and that HNO_3 dominated the Lake Tahoe Basin dry N deposition regime.

Jassby et al. (1994) estimated total dry deposition for the Tahoe watershed to be approximately $3.3 \text{ kg N ha}^{-1} \text{ year}^{-1}$, an estimate which falls in the lower half of the range we calculate for July through September. This suggests that total deposition taken on a yearly basis is substantially higher than previously considered. Fig. 4 compares dry N flux from summer and fall dry deposition to annual wet deposition (NADP, 1996; Jassby et al., 1994), and to annual estimates from more polluted sites in southern California (Bytnerowicz and Fenn, 1996).

Table 4

Ranges for NH_3 , HNO_3 , and NH_4NO_3 fluxes to forest canopies for the summer and fall dry season (July through September)

| N species | Lower limit (kg N ha^{-1}) | Upper limit (kg N ha^{-1}) |
|--------------------------|--|--|
| HNO_3 | 1.0 | 7.4 |
| NH_3 | 0.2 | 0.9 |
| NH_4NO_3 | 0.03 | 0.3 |
| Total | 1.2 | 8.6 |

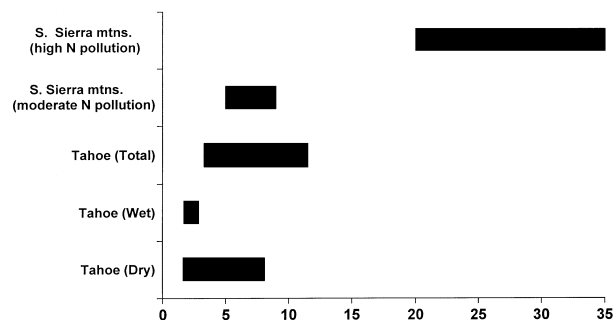


Fig. 4. Tahoe N deposition (wet, dry, total) compared to N deposition at moderately and highly polluted sites in the southern Sierra Nevada mountains.

While the Lake Tahoe Basin is not as polluted as some sites near Los Angeles, the ranges of N flux nonetheless equal those of moderately polluted sites (Bytnerowicz and Fenn, 1996; Taylor et al., 1997; Fenn et al., 1998).

4.3. Estimated flux to Lake Tahoe

Of the three quantified species, HNO_3 dominated N deposition to Lake Tahoe's surface, contributing more N ($27\text{--}34 \times 10^6 \text{ g}$), than NH_3 ($2.9\text{--}22 \times 10^6 \text{ g}$) or NH_4NO_3 ($0.11\text{--}4.9 \times 10^6 \text{ g}$). Total estimated deposition ranged $30 \times 10^6 \text{ g}$ to $61 \times 10^6 \text{ g}$ (Table 5). Thus the sum of this dry season N deposition is one-third of previous annual estimates for total dry N deposition to Lake Tahoe's surface (Reuter et al., 1998).

4.4. Implications

Moderate N deposition has long-term ecological implications for both terrestrial and aquatic ecosystems in the Lake Tahoe Basin. At the scale of the individual tree and in the short term, assimilated atmospheric N can directly benefit the plant. On an evolutionary time scale, plants have adapted to environments where N was available only through roots. Atmospheric deposition has increased on a much shorter, decadal time-scale, so foliar assimilation may constitute an additional stress to plants if they cannot physiologically assimilate N deposited to foliage (Taylor et al., 1994). Grulke et al.

Table 5

Ranges for direct NH_3 , HNO_3 , and NH_4NO_3 fluxes to Lake Tahoe surface water for the summer and fall dry season (July through September)

| N species | Lower limit ($10^6 \text{ g/kg N ha}^{-1}$) | Upper limit ($10^6 \text{ g/kg N ha}^{-1}$) |
|--------------------------|--|--|
| HNO_3 | 27/0.52 | 33/0.66 |
| NH_3 | 2.9/0.06 | 22/0.43 |
| NH_4NO_3 | 0.1/0.002 | 4.9/0.10 |
| Total | 30/0.57 | 61/1.2 |

(1998) and Dueck et al. (1998), for example, have linked increased N deposition to decreased root/shoot ratios, which may lead to nutrient imbalances in the plant. Also, anthropogenically produced particulate gases can reduce stomatal control over water loss, forcing early leaf senescence in drought-stressed conifers (Burkhardt and Reiner, 1994; Burkhardt et al., 1995). N deposition may thus contribute to forest health degradation in the Lake Tahoe Basin.

N deposition can degrade N retention for whole forest ecosystems as well, leading to eutrophication in adjacent aquatic ecosystems (Stoddard, 1991). In the more polluted European sites, the eastern United States, and southern California, high N loading from atmospheric deposition has led to a state of N saturation, where N supply from deposition exceeds N demand from the biological components of the ecosystem (Aber, 1992; Johnson, 1992). Ecosystems that are N saturated will 'leak' N to adjacent aquatic ecosystems, resulting in accelerated eutrophication over the long term (Stoddard, 1989; Aber, 1992). In an ecosystem as N limited as the Lake Tahoe Basin, however, moderate N loading over the short term (i.e. less than a decade) is unlikely to produce N saturation (McColl, 1982; Bytnerowicz et al., 1987; Fenn et al., 1998).

The consequences of continuous, moderate N deposition in the long term are less certain (Bytnerowicz and Fenn, 1996). Pulses of high N concentrations in spring runoff have been observed both in the Lake Tahoe Basin and in other subalpine watersheds (Goldman, 1988; Stoddard, 1991; Baron et al., 1994; Williams et al., 1995). Coats and Goldman (1993) observed that during a low-runoff summer following a dry winter, there was not only a pulse of N during the spring, but also after periods of heavy rain in the fall. Nitric acid easily washes off once deposited to the leaf surface (Cadle et al., 1991), so HNO_3 deposited to forest canopies can contribute to high N concentrations in runoff during such storms. From this, we hypothesize that N deposition to forest canopies as well as direct N deposition to water surfaces contribute N to Lake Tahoe's standing N pool, with eutrophication as a consequence. Better understanding of the consequences of such long-term inputs are uncertain and require measurement that is similarly long term.

5. Summary and conclusions

In this preliminary study, we observed elevated ambient HNO_3 concentrations to approach 26 nmol N m^{-3} during the day, and 11 nmol N m^{-3} night during the dry season, leading to substantial N deposition to both lake and forest canopies, ranging from 1.0 to 7.4 kg N ha^{-1} . Calculated canopy compensation point exceeded NH_3 concentrations, suggesting negligible forest canopy N

deposition (as NH_3). Consistent with its small V_d and low concentrations, N flux due to NH_4NO_3 to forest canopies was also small (0.1 – $4.9 \times 10^6 \text{ g N}$).

Nitric acid and NH_3 dominated N flux to Lake Tahoe surface water, delivering 27 – $34 \times 10^6 \text{ g}$ and 2.9 – $22 \times 10^6 \text{ g}$ during the 3-month dry season. Ammonium nitrate deposition to the Lake was relatively unimportant, contributing at most $4.9 \times 10^6 \text{ g N}$ over the course of this dry season. Total summer/fall contributions from all three species to the lake surface accounts for one-third of annual dry N deposition estimates by Reuter et al. (1998).

Estimated dry N flux to forest canopies from all N-containing species, on the other hand, totaled 3.2 – 7.6 kg N ha^{-1} for the summer and fall dry season, exceeding the $3.3 \text{ kg N ha}^{-1} \text{ year}^{-1}$ estimate proposed by Jassby et al. (1994). The range for total flux to the Lake Tahoe Basin watershed (wet plus dry = 3.3 – $14 \text{ kg N ha}^{-1} \text{ year}^{-1}$) was comparable to that at moderately polluted sites in southern California (5 – $9 \text{ kg N ha}^{-1} \text{ year}^{-1}$) (Fig. 4).

These results suggest that dry N deposition is more important than wet deposition for forest canopies in the Lake Tahoe Basin, and at least as important as wet deposition for direct N loading to the lake. In more productive ecosystems, moderate N pollution would not be a threat to ecosystem health. However, Lake Tahoe's unique clarity and the N-limited forest ecosystem are inherently vulnerable to N deposition in the long term. As with other sites in the Sierra Nevada Mountains, dry N deposition dominates the transfer of N from the atmosphere to the watershed, and the biology of forest canopies appears to mediate the bulk of that transfer via NH_3 compensation points and the increased surface area of tree canopies.

5.1. Further research

If HNO_3 and NH_3 are the most important contributors to the loading of atmospheric N to the terrestrial and aquatic ecosystems in the Lake Tahoe Basin, then they should be closely monitored on a long-term basis. If the relative importance of HNO_3 , NH_3 , and NH_4NO_3 (to each other and to wet deposition) suggested by this study are to be confirmed with empirical data, a network of sample sites should be set in place and maintained long enough to assess spatial and temporal variability as well as long-term trends. In addition to identifying sources, future attempts to more accurately quantify deposition and its effects should include: (1) additional ambient measurements at additional sites in the Lake Tahoe Basin; (2) assessment of the role of biology in the transfer of N to forest ecosystems (i.e. V_g , LAI, and compensation points); and (3) evaluation of subsequent transfers of N to the aquatic ecosystems (i.e. N pulses in runoff).

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